Tetrahedron, 1966, Vol. 22, pp. 167 to 173. Pergamon Press Ltd. Printed in Northern Ireland

LOW-TEMPERATURE OPTICAL ROTATORY DISPERSION*

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(*Received* 2 *August* 1965)

Abstract—A technique for measuring optical rotatory dispersion between room temperature and −185° is described. ORD curves of (+) camphor, (−) *trans*-β-hydrindanone, ergosterol, (−) α-phellandrene and (+) butanol-2 at room and lower temperatures are given, together with a short discussion.

INTRODUCTION

OPTICAL rotatory dispersion (ORD) and circular dichroïsm (CD) are closely related phenomena. From the knowledge of one of them over the entire spectral range, the other can be calculated with the aid of the Kramers–Kronig relations. Since only a limited part of the spectrum lies within the range of present-day instruments, a combined use of ORD and CD is necessary for obtaining a maximum of information. The relative advantages of one over the other have been discussed in some detail.[1,2] Background effects and plain curves can only be studied by ORD technique. Another advantage of ORD is the greater sensitivity of present-day spectropolarimeters as compared to CD instruments, especially if small effects have to be studied.

Until now CD was in a better position as to the possibility to extend the measurements down to liquid-nitrogen temperatures.

In recent years several authors have shown that variable temperature CD-measurements may shed light upon conformational and solvation equilibria.[3–6]

In the present paper a technique for measuring ORD at variable temperatures is reported, the lowest temperature attainable being −185°.

As an illustration of the potentialities of this technique the low-temperature ORD curves of the following compounds are given: (+) camphor, (−) *trans*-β-hydrindanone, ergosterol, (−)α-phellandrene and (+) butanol-2.

EXPERIMENTAL

A. *Construction of the apparatus* (Fig. 1)

In low-temp ORD-measurements a major problem is the avoidance of all birefringence and depolarization in the light path. Therefore the windows of the measuring-cell have to be free from strain. To achieve this we have chosen a construction, in which a strain-free cylindrical quartz cell is cooled in a stream of N_2. For that purpose the cell is surrounded by an insulating vessel. The light passes through holes in the vessel closed by quartz windows that are connected to the walls of the vessel very loosely, so that no strain is introduced.

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* A preliminary account of this work has been given in *Tetrahedron Letters* 3037 (1965).

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[5] G. Snatzke, D. Becher and J. R. Bull, *Tetrahedron* **20**, 2443 (1964).

[6] K. M. Wellman, W. S. Briggs and C. Djerassi, *J. Amer. Chem. Soc.* **87**, 73 (1965).

The outer wall is made of pertinax. The insulating material is some variety of foam plastic (tempex), the same type as used in refrigerators. The quartz cell is placed in a hollow stand (brass) connected to the brass bottom of the inner vessel.

The inner vessel is filled with liquid nitrogen. Almost at the bottom a 100 Ω resistor is placed. This can dissipate 0–20 Watts depending on the voltage applied. With no voltage applied, the temp of the cell (measured with a Cu–Co-thermocouple) becomes −145°. With N_2 boiling at a high rate, the cell is cooled down to −185°. The region −145° to −185° is readily accessible by varying the voltage applied to the resistor. When the inner vessel is only half filled, the N_2 gas can be warmed up by a second resistor, placed as shown in the Fig. In this way the temp range between −145° and −100° is covered. For the range room temp to −100° precooled N_2 gas is blown in.

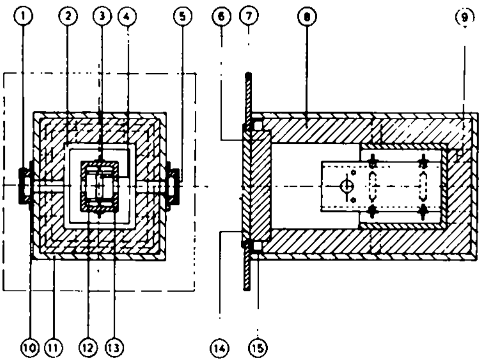

FIG. 1. 1. Brass cover, slipping over the brass housing of the window.
Keeps the quartz window in place without exerting pressure.
2. Inner vessel (brass).
3. Bushing insulator (teflon).
4. Resistors (100 Ω).
5. Quartz window.
6. Insulating material (tempex).
7. Brass support connected to the outer vessel.
8. Insulating material (tempex).
9. Supports for the inner vessel (wood cut across grain).
10. Brass housing of the quartz window.
11. Outer vessel (pertinax).
12. Brass bars supporting the quartz cell.
13. Hollow stand (brass).
14. Cover (pertinax).
15. Brass connection between 7 and 11.

To avoid condensation of water on the outer surface of the quartz windows, these are heated by a heating wire, fitted in the brass housing of the windows.

To maintain a constant temp, the level of the liquid N_2 should be constant. This is achieved by using a resistance with negative temp coefficient (NTC) just dipping into the liquid N_2. This NTC is part of a Wheatstone bridge. If the level becomes too low, the NTC is no longer cooled by the liquid N_2 and the resistance alters. The bridge goes off balance and a voltage difference is produced. Liquid N_2 is introduced into the vessel either manually or automatically until the bridge is balanced again.

This variable temp cell can also be used for absorption spectra and CD-measurements.

High-temp ORD, CD and absorption measurements are performed with a similar apparatus. Again a 2-cm strain-free cylindrical quartz cell is placed in an insulating vessel. The outer wall is pertinax; the cylindrical inner vessel, made of brass, is wound with heating wire, allowing measurements between room temp and +175°. The insulating material is asbestos.

The spectropolarimeter used, employs the Faraday effect both for modulation and for compensation. The electronic part consists essentially of an ETL-NPL automatic polarimeter control unit type 143 A. The optical system has been built in this department. A monochromatic light beam is obtained with a 900 W Xenon lamp (Osram XBO 1001) and a 500 mm Bausch and Lomb grating monochromator. The polarizers are Glan prisms of calcite; the Faraday rotation is generated in fused-quartz bars. The fotomultiplier is an EMI type 6256 B. The compensating current passes through a variable resistance (Philips Universal programme transmitter PR 7211), of which the ohmic value changes synchronously with the scanning of the wavelengths in such a manner that at each wavelength it is proportional to the Verdet constant of the quartz. The voltage over this resistance was recorded during the wavelength-scanning and in this way a plot of rotation versus wavelength was obtained.*

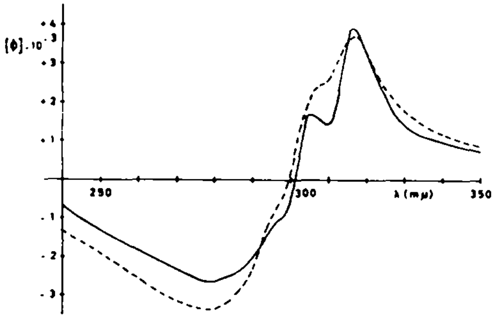

FIG. 2. Molecular rotation of (+) camphor in EPA at 20° (- - -) and at −155° (———).

B. *Solvents*

The solvents used are: EPA (5 ether, 5 isopentane, 2 alcohol); MIP (1 methylcyclohexane, 4 isopentane; PIP (5 propane, 1 isopentane).

EPA is an excellent solvent for most purposes, but it has the disadvantage of becoming very rigid at low temp. This may introduce strain in the glass, so that measurements become impossible because of birefringence.

MIP is a very soft glass, down to −190°.

PIP remains a liquid even at liquid N_2. This has the advantage that the establishment of conformational equilibria is not hampered by the rigidity of the medium.

All measurements are corrected for volume contraction; the influence of the index of refraction is neglected.

RESULTS AND DISCUSSION

(+) *Camphor* in EPA (Fig. 2) shows a sharpening of the fine-structure and a diminishing of the amplitude at −155°. The circular dichroïsm in MIP at −192°[4] is smaller than at 20°; this has been ascribed to solvation effects†. The gas-phase ORD at 180° has been measured over 30 years ago.[7]

(−) *trans-β-Hydrindanone*. The vibrational structure of this compound has been extensively studied in different solvents at room temp.[8] It is supposed that no con-

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* The authors are indebted to Mr W. Wladimiroff for his advice with respect to the automatization of the spectro-polarimeter.

† A theory, not based on conformational or solvation equilibria, of the influence of temp on the optical activity of molecules exhibiting low circular dichroïsm was put forward by O. E. Weigang, jr, *J. Chem. Phys.* 42, 2244 (1965).

[7] T. M. Lowry, *Optical Rotatory Power.* Longmans Green London (1935) and Dover publications, New York (1964).

[8] R. Deen, Thesis Leiden (1961).

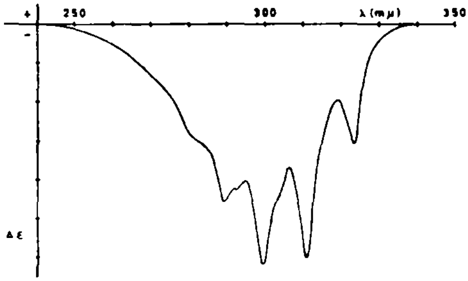

Fig. 3. Circular dichroism (in arbitrary units) of (—) *trans*-β-hydrindanone in the gasphase at 92°, identical with the CD of the same compound at 20° in MIP.

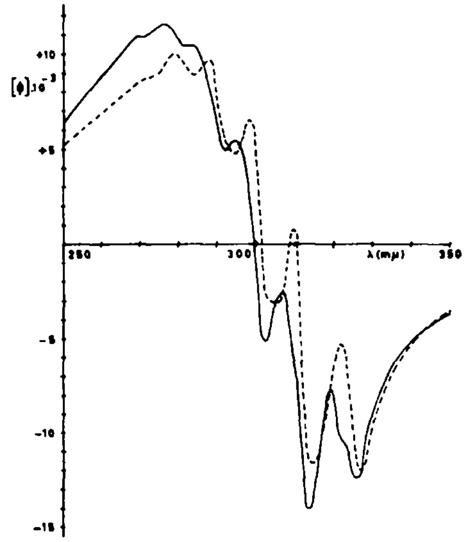

Fig. 4. Molecular rotation of (—) *trans*-β-hydrindanone in MIP at 20° (- - -) and at −140° (———).

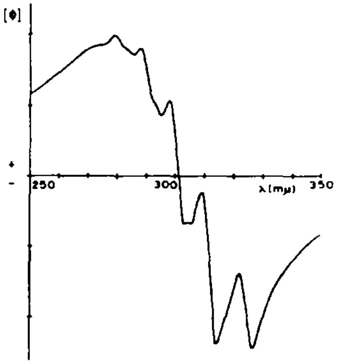

Fig. 5. Optical rotation (in arbitrary units) of (—) *trans*-β-hydrindanone in the gasphase at 90°.

formational mobility is present. The CD of a solution in MIP at 20° is identical for wavelength-position of the maxima and form of the curve with the gasphase CD at 92°* (Fig. 3). The ORD of a solution in MIP at 20° (Fig. 4) is nearly identical in the same respects with the gasphase ORD at 90° (Fig. 5). From this it is concluded that in this solvent we observe the unsolvated species. When a solution in MIP is cooled to −140°, shoulders appear in the ORD on the short-wavelength side of the long-wavelength troughs and the fine-structure of the short-wavelength peaks is blurred (Fig. 4). This can be explained by assuming an equilibrium between solvated and unsolvated molecules, the solvated ones showing a blue-shift of their $n \rightarrow \pi^*$ transition.

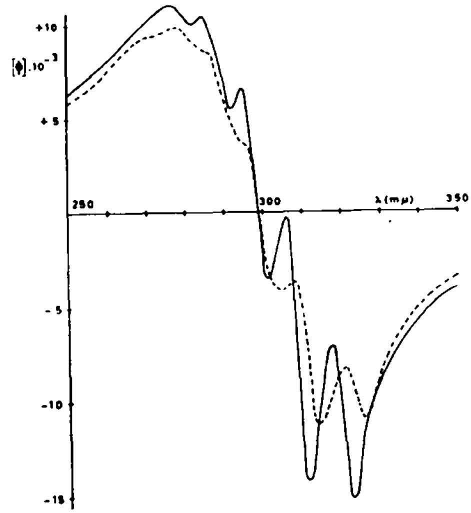

Fig. 6. Molecular rotation of (−) *trans*-β-hydrindanone in EPA at 20°C (- - -) and at −145° (———).

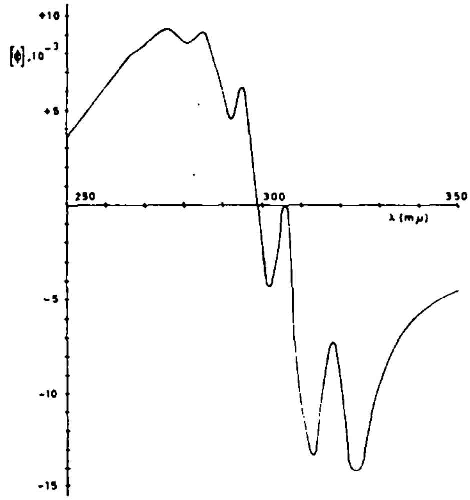

Fig. 7. Molecular rotation of (−) *trans*-β-hydrindanone in PIP at −170°.

* CD measurements were performed with a dichrographe (Roussel-Jouan).

While the more polar EPA solution shows loss of vibrational structure at room temp, cooling to −145° gives a better resolved spectrum (Fig. 6), which resembles strongly the −170° spectrum in PIP (Fig. 7). The vibrational structure is as pronounced as in MIP at 20°, but there is a slight change in the form of the ORD spectrum, which is shifted to shorter wavelengths.

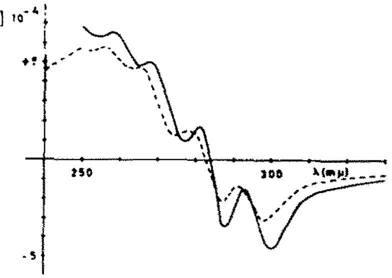

FIG. 8. Molecular rotation of ergosterol in MIP at 20° (- - -) and at −145° (———).

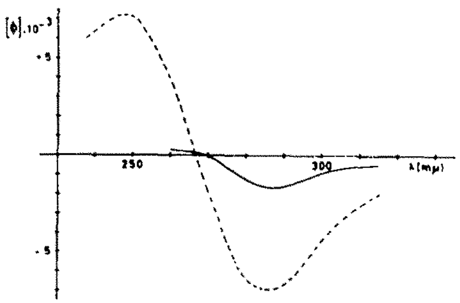

FIG. 9. Molecular rotation of (−) α-phellandrene in MIP at 20° (- - -) and at −150° (———).

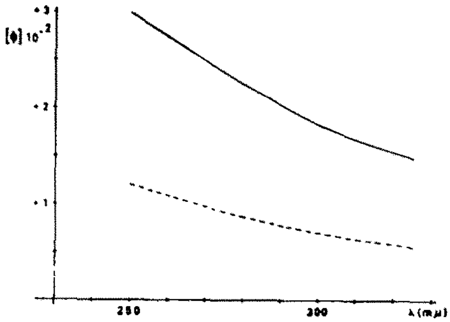

FIG. 10. Molecular rotation of (+) butanol-2 in EPA at 20° (- - -) and at −150° (———).

Ergosterol[8–10]. An increase in rotational strength and a small redshift is observed on cooling to −145° in MIP (Fig. 8).

(−)*α-Phellandrene*[8,9]. The molecular rotation decreases drastically at lower temps (Fig. 9). No shift in the wavelength of the trough can be detected. An increase of the

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[9] R. Deen and H. J. C. Jacobs, *Proc. Koninkl. Acad.* **B64**, 313 (1961).

[10] H. J. C. Jacobs and E. Havinga, *Rec. Trav. Chim.* **84**, 932 (1965).

rotation at 320 mμ has been observed at 80° as compared to room temp.[11] The simplest explanation is a conformational equilibrium. It should be noted that the CD apparatus is not sensitive enough to give reliable measurements of (—)α-phellandrene at low temperatures.

(+) *Butanol-2**. The absorption maximum of this compound lies in the UV region, not accessible to CD measurements. The measurement of the plain curve at $-150°$ shows a marked increase of the optical rotation with respect to room temp (Fig. 10). A decrease of the rotation of a butanol-2 solution in cyclohexane upon heating from 20 to 70° has been reported.[12] This temp dependence of the optical rotation is probably due to a conformational equilibrium of the different rotational isomers of butanol-2.

* Kindly supplied by Mr H. L. Boter, Chemical Laboratory of the National Defence Research Organization T.N.O., Rijswijk Z. H., The Netherlands.

Acknowledgement—One of the authors (C. A. E.) is indebted to the Netherlands Organization for the Advancement of Pure Research (Z. W. O.) for the sponsorship of his study on optical activity performed under the auspices of the Netherlands Foundation for Chemical Research (S. O. N.).

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[12] H. J. Bernstein and E. E. Pedersen, *J. Chem. Phys.* **17**, 885 (1949).